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The influence of the type of accelerant, type of burned material, time of burning and availability of air on the possibility of detection of accelerants traces

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Abstract

The presented research consisted in a series of field experiments and laboratory analyses of obtained samples. Their aim was to investigate how different factors influence the possibility of identification of accelerant traces in conditions that are as similar as possible to those of real fires. The studied factors were: type of burned material, type of accelerant, length of time between lighting and extinguishing of fire and the air availability level. The obtained results show that, among investigated factors, the type of burned material has the greatest influence. The other factors, with regard to their influence, could be ranked in descending order as follows: ‘other’ (hard to determine and regulate factors), type of accelerant, time of burning and air availability. ‘Other’ factors include arrangement of the burned material and dispersion of the accelerant.

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1. Introduction

The chemical analysis of fire debris with the aim of potential accelerant detection is not a new issue, and there are many publications on this subject. Many of them emphasize that accelerant traces isolated from fire debris significantly differ from ‘fresh’ liquids because of processes (e.g. evaporation and pyrolysis) and factors which occur in conditions typical of a fire. Surprisingly, only a few authors have made an attempt to reconstruct these conditions in order to investigate how each of them influences the results of analysis and which of them is the most important. So far, most experiments have been carried out on a laboratory

scale [1–3]; there is only one paper published, which describes a full-scale fire experiment [4].

This noted lack of field experiments might stem from the fact that they are problematic and regulating the factors that have an effect in such circumstances is difficult, if not impossible. Therefore, obtained results are sometimes hard to explain and interpret. To the best of the authors’ knowledge, up till now field experiments have not been carried out in order to investigate the influence of factors such as type of accelerant used, type of burned material, time between starting and extinguishing of the fire and availability of air on the possibility of detection of accelerants traces. The presented experiments constitute an attempt to fill this gap.

Although studying the influence of the above mentioned factors did not directly lead to any advances in methods of

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chemical analysis of accelerant traces, it did broaden our knowledge of accelerant-related fires. It also provided us with some practical knowledge, such as what kind of material retains the maximal amounts of accelerant traces, and thus what should be collected as a sample, if there is such a choice.

Samples were prepared for chromatographic analysis by the headspace method with passive adsorption of analytes on Tenax TA[®]. Analysis was carried out using an automatic thermal desorber connected to a gas chromatograph coupled with a mass spectrometer.

2. Experimental

2.1. Instrumentation

- (a) An automated thermal desorber—ATD Turbo Matrix (Perkin-Elmer Instruments, USA) with a module enabling the focusing of analytes on a ‘cold trap’ and a set of pre-packed adsorption tubes (SUPELCO) containing Tenax TA were used for analytes adsorption and thermodesorption.
- (b) An Auto System XL gas chromatograph (Perkin-Elmer Instruments) coupled with a Turbo Mass Gold mass spectrometer (Perkin-Elmer Instruments) was employed for chromatographic analysis. A 30 m long Elite 1 capillary column with an inner diameter of 0.25 mm and stationary phase film thickness of 1 µm was utilised. The mass spectrometer was equipped with a quadrupole analyser and electron impact ionisation. The ionisation energy was set at 70 eV and the total ion measurement mode was used.

2.2. Materials and reagents

The following materials and reagents were used:

- Set of pre-packed stainless steel adsorption tubes (SUPELCO), containing Tenax TA[®] were used for analytes passive adsorption.
- Twist-type jars of 750 cm³ capacity were used to collect the samples.
- Helium (Helium 6.0 Linde Gas AG, Germany) was used as a carrier gas in chromatography.
- Five different types of flammable liquids—extraction solvent (by DRAGON), gasoline (by ORLEN), universal diluter (by DRAGON), kerosene (by DRAGON) and diesel fuel (by ORLEN), were used as accelerants in the conducted field experiments. They were obtained from the local gasoline service station and chemist shops.
- Three different types of combustible material, typically used in home interiors—polyolefin carpet (cut up into pieces approximately 20 cm × 15 cm), deciduous wood logs (30 cm long) and pieces of unpainted chipboard (10 cm × 20 cm × 1.2 cm) were used in field experiments.

2.3. Analytical procedure

The following analytical procedure was established on the basis of previously conducted optimization research [5]:

The analyzed sample is placed in a glass jar with three adsorption tubes. It is heated at 60 °C for 16 h. Compounds adsorbed on Tenax TA are then thermodesorbed (conditions: 335 °C for 20 min) with the use of a thermal desorber and concentrated on a cold trap—a quartz tube containing a small quantity of Tenax TA and cooled to –30 °C. Afterwards, they are quickly thermodesorbed again (conditions: 335 °C for 20 min) and carried to a gas chromatograph through a hot transfer line (200 °C).

For the identification of analytes, a gas chromatograph hyphenated with a mass spectrometer is used.

GC-MS analysis was conducted according to the following temperature program: initial temperature 30 °C maintained for 3 min; increase 5 °C/min to 120 °C; increase 15 °C/min to 270 °C; final temperature 270 °C maintained for 2.5 min.

Helium was used as a carrier gas, its pressure regulated in order to achieve the following flow values: the flow of carrier gas during thermodesorption, 30 cm³/min; the flow of gas diluting the carrier gas after thermodesorption from the cold trap (outlet split), 30 cm³/min; the flow of gas diluting the carrier gas after thermodesorption from the adsorbent (inlet split), 8 cm³/min.

If the analytes concentration was too high to obtain a chromatogram with properly separated peaks, samples were reanalyzed with adequately higher split settings (inlet only or inlet and outlet).

2.4. Experiments description

The research concerning the influence of time of burning, type of accelerant and type of burned material on the possibility of detection and identification of accelerant traces involved examination of three kinds of combustible materials (carpet, deciduous wood and chipboard) and five different accelerants (extraction solvent, gasoline, universal diluter, kerosene and diesel fuel).

The experiments concerning carpet were conducted as follows: eight pieces of examined carpet were placed in each of five open cylindrical containers which were 45 cm in diameter and 50 cm high. The containers were placed in a poorly ventilated room. Prior to burning, approximately 250 cm³ of the appropriate accelerant was poured onto the investigated material. After a fixed period of time, the fire was extinguished using water and one sample was taken from each container.

Each sample was placed in a clean and airtight glass jar, and, after being delivered to the laboratory, analyzed three times (three adsorption tubes were placed in each jar).

Experiments were conducted on samples exposed to 20, 30, 40, 50, 60, 70 and 80 min of burning.

One blank sample was analyzed with each set of samples. In order to prepare the blank sample, three adsorption tubes were placed in an empty glass jar, exactly like the ones used for samples collection. The jar was shut, heated and then the adsorbed compounds were analyzed using GC-MS.

It was noticed that after 40–50 min, the flames extinguished and after that the burned carpet was only smoking slightly.

Analysis of chromatograms obtained showed that significant changes in patterns characteristic of applied accelerants occur if the burning time is longer than 50 min. That is why when the described experiments were repeated, and when they were carried out with the remaining combustible materials (deciduous wood and chipboard), duration of burning was 50, 60 and 70 min. In this way, for each condition (time of burning, kind of accelerant and burned material), six results of analysis were obtained (two independent experiments, one sample each, every sample analysed three times).

For each experiment, only one sample was taken, because, after burning, the amount of remaining material was so small that sometimes all the material was taken as a sample.

For burned materials (carpet, wood and chipboard), the same time of burning was used to enable comparison of results and to determine the differences in properties of these materials.

Some of the preliminary experiments (burning of the carpet samples for 20, 30, 40 and 80 min) were not repeated, because their results were only needed in order to establish the optimal time of burning for ‘real’ experiments.

The experiments involving wood and chipboard were conducted in the same manner as the “carpet” experiment, whereby five logs of wood or six pieces of chipboard were placed in each container.

Wood extinguishes spontaneously after 35–45 min and chipboard after 15–25 min. The smoldering debris was extinguished by water.

In the experiments concerning the influence of air availability on the results of fire debris analysis, carpet was used as the combustible material.

It was set on fire using each of five accelerants (extraction solvent, gasoline, universal diluter, kerosene and diesel fuel) and extinguished by water 60 min after ignition.

The combustion was conducted in three different conditions of air availability.

Each burning (specific air availability, burned material and accelerant) was performed twice. Firstly, the containers were placed in a poorly ventilated room just as described earlier. Increased air availability was obtained by placing the containers outside, in the open air. A further increase in air availability was gained by arranging the burned material in piles on the concrete ground in the open air, without using any containers.

Samples were collected in clean, airtight jars. Upon delivery to the laboratory, each sample was analyzed three

times (three adsorption tubes were placed in each jar). In this way, for each experiment (specific air availability, burned material and accelerant), six analysis results were obtained.

3. Results and discussion

Example chromatograms obtained as a result of experiments concerning the influence of time of burning, type of accelerant and type of burned material are shown in Figs. 1–5.

Comparison of example chromatograms for each of the three levels of air availability and each of five investigated accelerants is presented in Figs. 6–10.

3.1. Experiments involving the burning of carpet using different accelerants and for different burning durations

It was found that for all examined accelerants, except the extraction solvent, characteristic patterns are recognizable for all investigated periods of time. In the case of the extraction solvent (the most volatile mixture among those employed), the characteristic profile of compounds is recognizable only for the shortest burning time period (20 min).

For all accelerants, with prolonged time of burning, the chromatograms changed and became similar to standard chromatograms obtained for highly evaporated flammable liquids; however, some irregularities can be observed in the described trend.

Chromatograms obtained for the same sample are consistent with each other in pattern (relative quantitative ratios of isolated compounds) as well as in signal level. Chromatograms obtained for repetitions of experiments significantly differ from results of experiments carried out for the first time.

It was observed that a shield of charred material arose on the surface of the burning carpet. Beneath this shield, uncharred material remained, even after the fire self-extinguished. This spontaneous process of separation of the deeper layers of fire debris is probably the reason why traces of most accelerants in burned carpet samples are easily recognizable, irrespective of time between ignition and extinguishing of fire.

3.2. Experiments involving the burning of deciduous wood logs using different accelerants and for different burning durations

The signal level for most of the samples was beneath the detection limit for accelerant traces. The detection limit was established to be 6×10^9 mV, on the basis of the results of blank samples analysis (for the lowest split settings used, which were: inlet split = $7 \text{ cm}^3/\text{min}$ and outlet split = $30 \text{ cm}^3/\text{min}$).

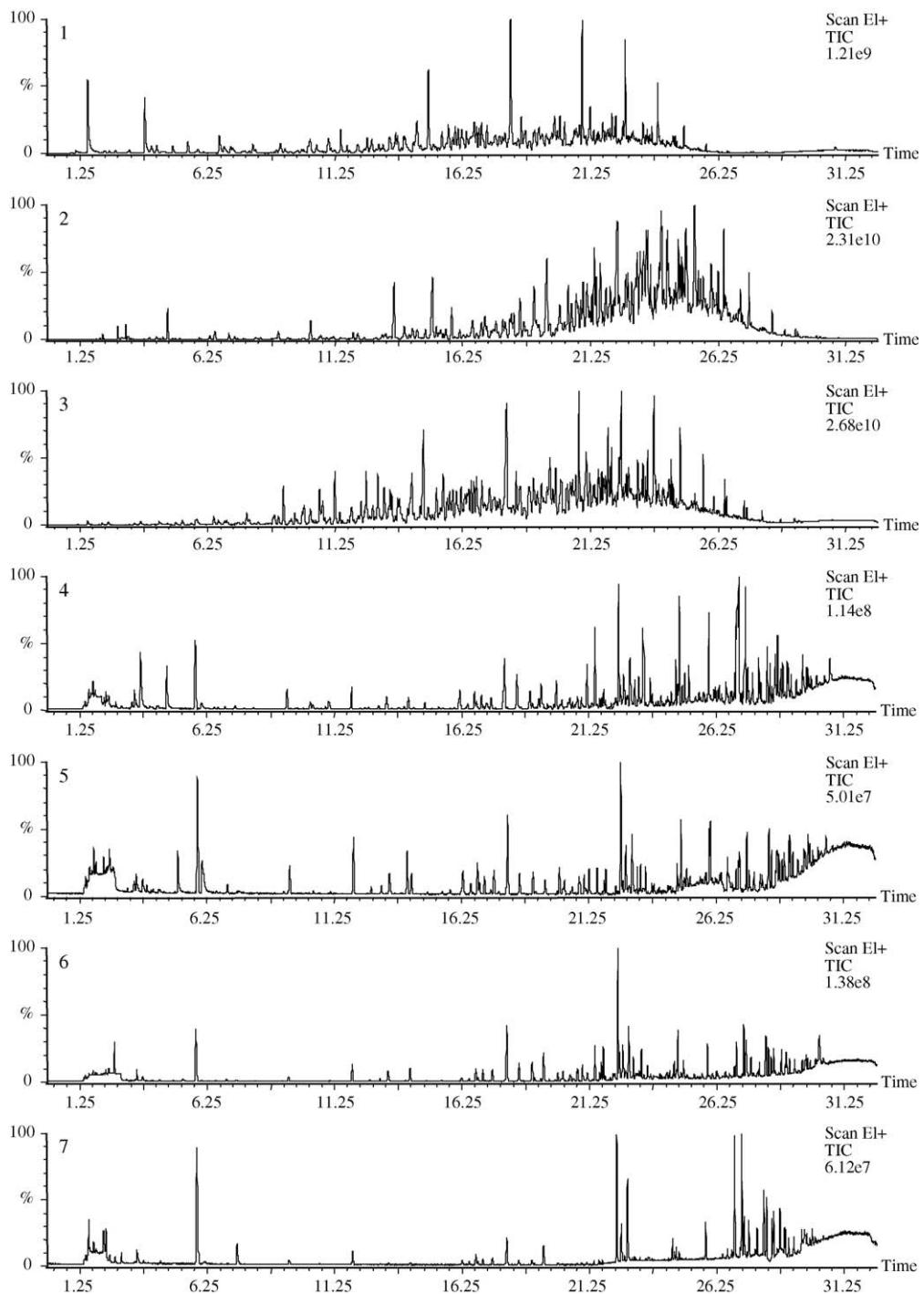


Fig. 1. Standard chromatogram of diesel fuel (chromatogram 1) and exemplary chromatograms obtained as a result of analysis of remains of different combustible materials ignited using diesel fuel as an accelerant. Chromatograms 2 and 3—carpet extinguished after adequately 50 and 70 min; chromatograms 4 and 5—deciduous wood extinguished after adequately 50 and 70 min; chromatograms 6 and 7—chipboard extinguished after adequately 50 and 70 min.

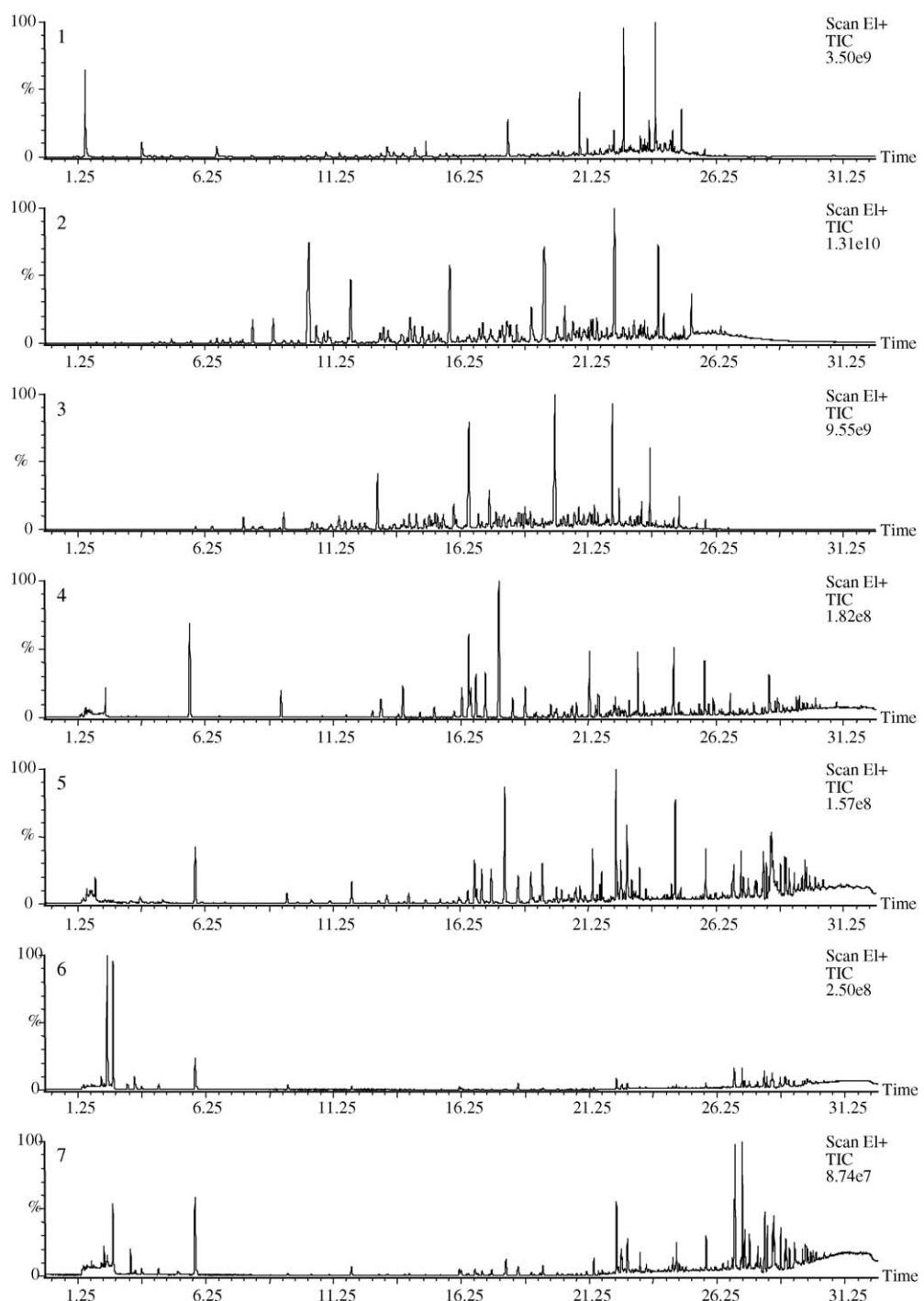


Fig. 2. Standard chromatogram of kerosene (chromatogram 1) and exemplary chromatograms obtained as a result of analysis of remains of different combustible materials ignited using kerosene as an accelerant. Chromatograms 2 and 3—carpet extinguished after adequately 50 and 70 min; chromatograms 4 and 5—deciduous wood extinguished after adequately 50 and 70 min; chromatograms 6 and 7—chipboard extinguished after adequately 50 and 70 min.

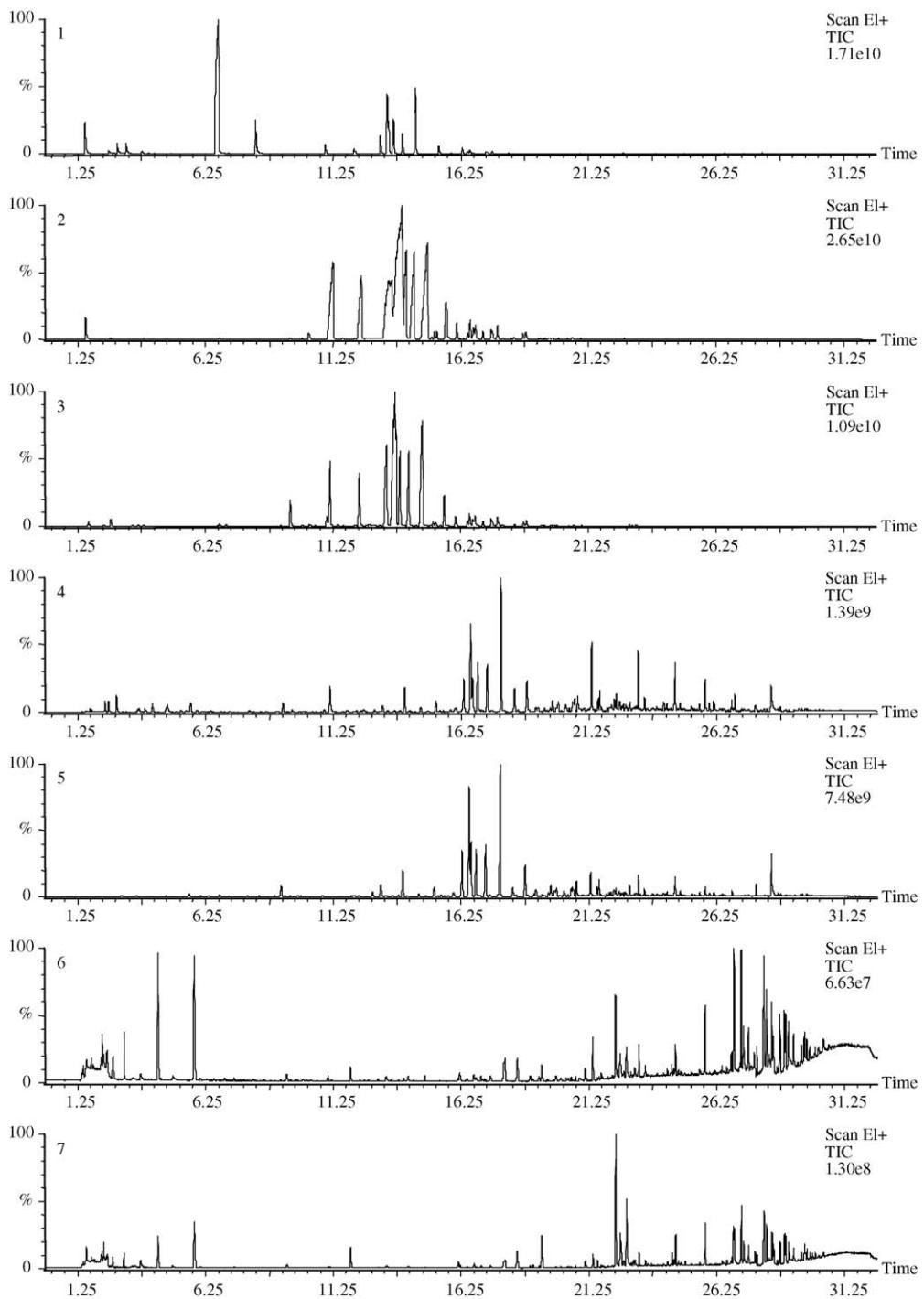


Fig. 3. Standard chromatogram of universal diluter (chromatogram 1) and exemplary chromatograms obtained as a result of analysis of remains of different combustible materials ignited using universal diluter as an accelerant. Chromatograms 2 and 3—carpet extinguished after adequately 50 and 70 min; chromatograms 4 and 5—deciduous wood extinguished after adequately 50 and 70 min; chromatograms 6 and 7—chipboard extinguished after adequately 50 and 70 min.

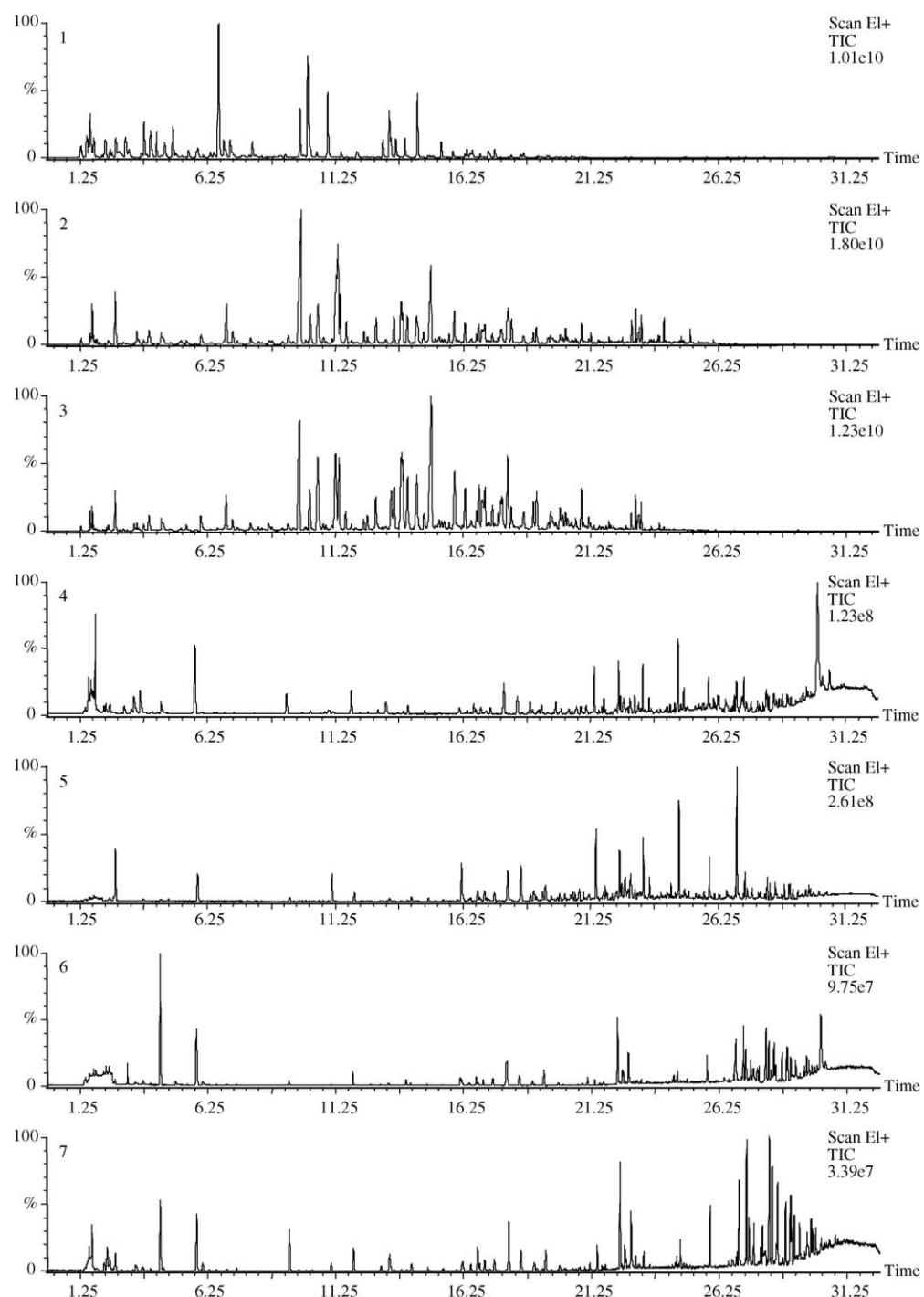


Fig. 4. Standard chromatogram of unleaded gasoline (chromatogram 1) and exemplary chromatograms obtained as a result of analysis of remains of different combustible materials ignited using unleaded gasoline as an accelerant. Chromatograms 2 and 3—carpet extinguished after adequately 50 and 70 min; chromatograms 4 and 5—deciduous wood extinguished after adequately 50 and 70 min; chromatograms 6 and 7—chipboard extinguished after adequately 50 and 70 min.

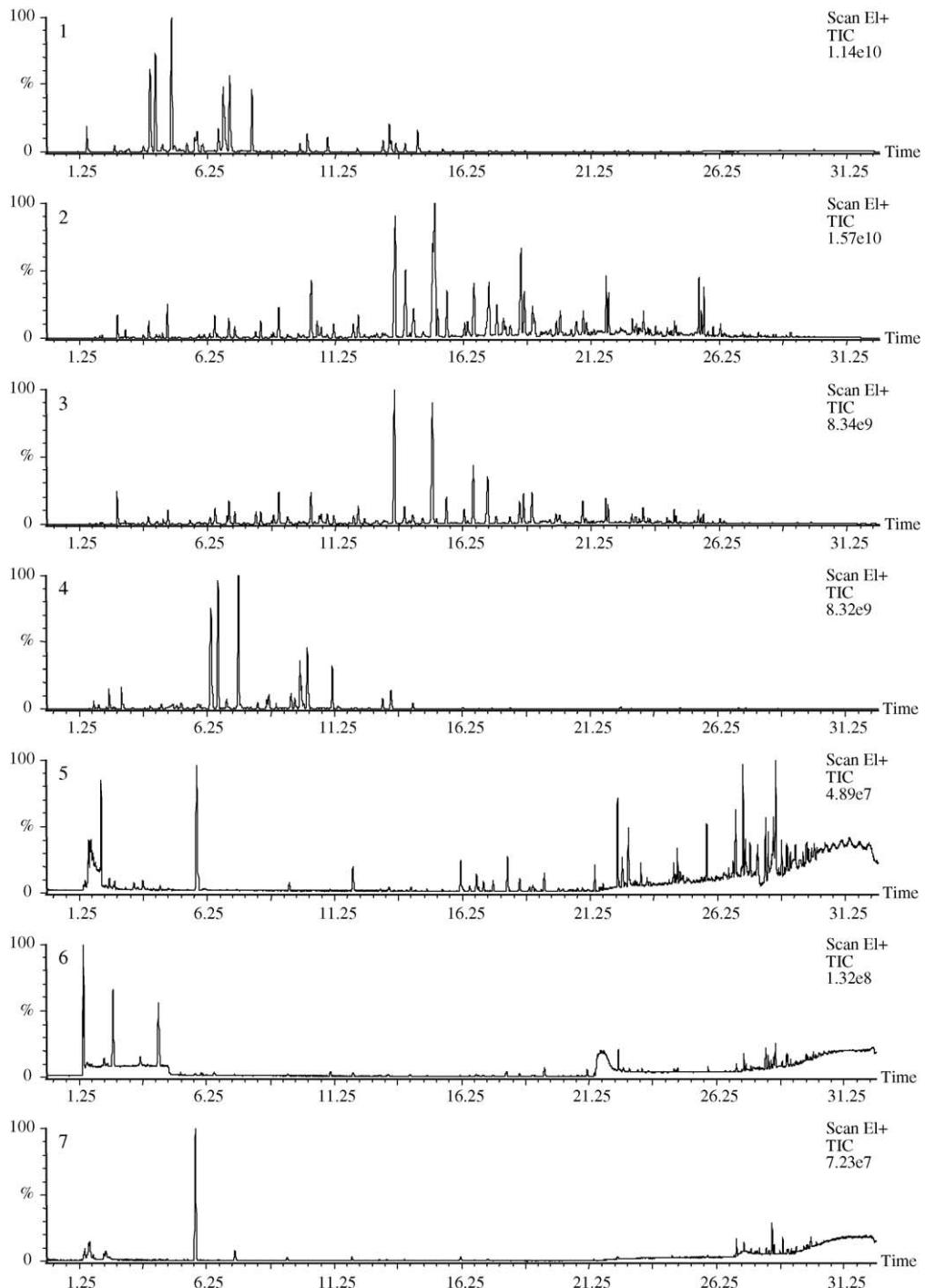


Fig. 5. Standard chromatogram of extraction solvent (chromatogram 1) and exemplary chromatograms obtained as a result of analysis of remains of different combustible materials ignited using extraction solvent as an accelerant. Chromatograms 2 and 3—carpet extinguished after adequately 50 and 70 min; chromatograms 4 and 5—deciduous wood extinguished after adequately 50 and 70 min; chromatograms 6 and 7—chipboard extinguished after adequately 50 and 70 min.

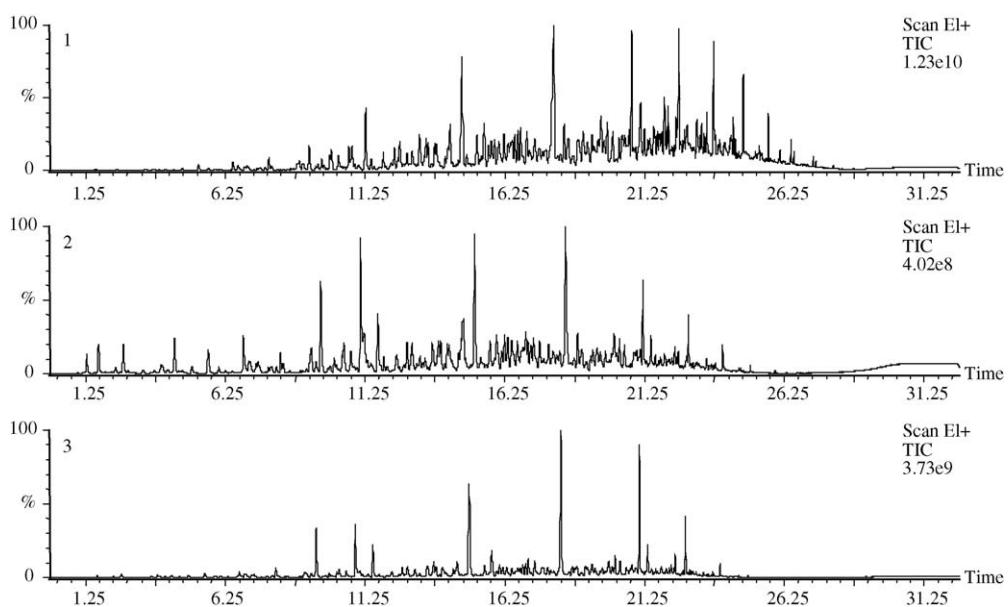


Fig. 6. Exemplary chromatograms obtained as a result of analysis of remains of carpet ignited using diesel fuel and distinguished by water after 60 min. Burning was conducted at three different levels of air accessibility—lowest (chromatogram 1), medium (chromatogram 2) and highest air accessibility (chromatogram 3).

On the chromatograms where the signal level is lower than the detection limit, signals of alkyl derivates of benzene can be observed. Their quantitative ratios are very similar to those of some generally available solvents (such as “universal diluter” by DRAGON). This effect cannot be

observed if analysis is conducted using a flame ionization detector (FID), due to its higher detection limit [5].

The results of experiment repetitions slightly differ from the results obtained from the first experiments, but the general profiles of compounds remain constant.

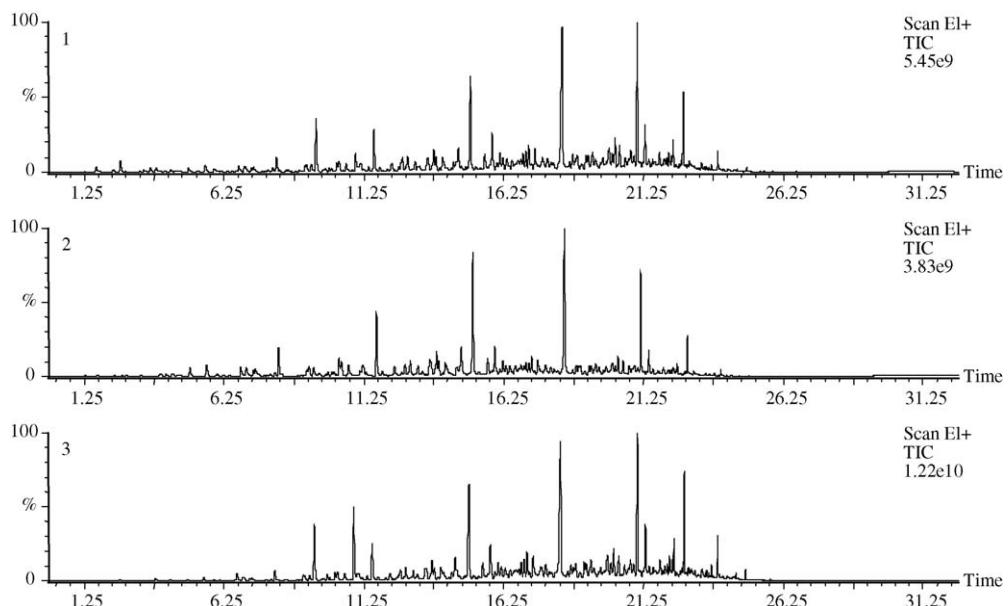


Fig. 7. Exemplary chromatograms obtained as a result of analysis of remains of carpet ignited using kerosene and distinguished by water after 60 min. Burning was conducted at three different levels of air accessibility—lowest (chromatogram 1), medium (chromatogram 2) and highest air accessibility (chromatogram 3).

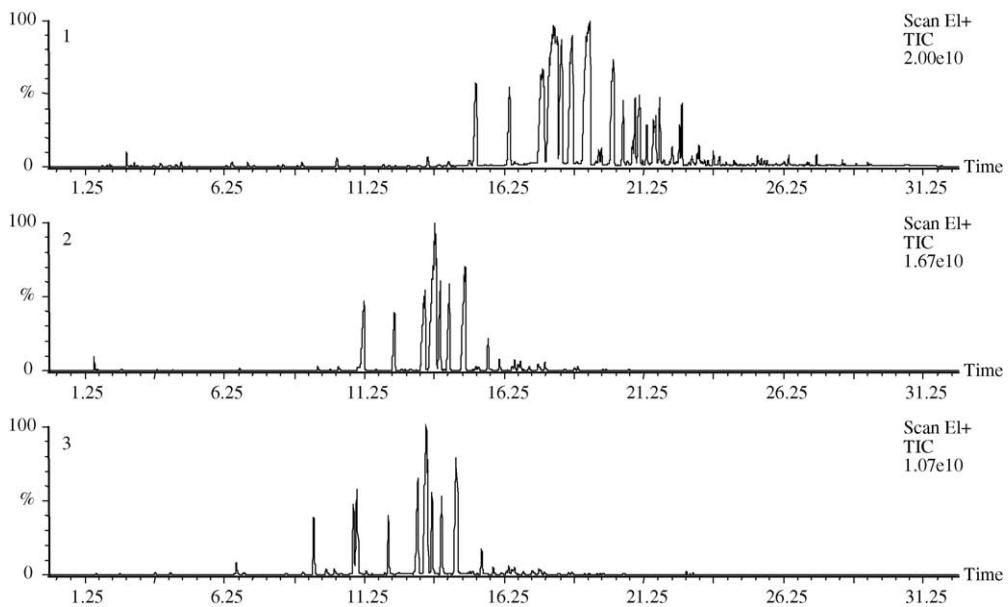


Fig. 8. Exemplary chromatograms obtained as a result of analysis of remains of carpet ignited using universal diluter and distinguished by water after 60 min. Burning was conducted at three different levels of air accessibility—lowest (chromatogram 1), medium (chromatogram 2) and highest air accessibility (chromatogram 3).

As for the samples whose signal level exceeds the detection limit (universal diluter 60 min; universal diluter 70 min; extraction solvent 50 min), the traces of used accelerant are easily recognizable. There is no significant relationship

between time of burning and accelerants traces detectability. This indicates that the determinative influence on the amount of accelerants remnants have other parameters such as the arrangement of burned material in the container.

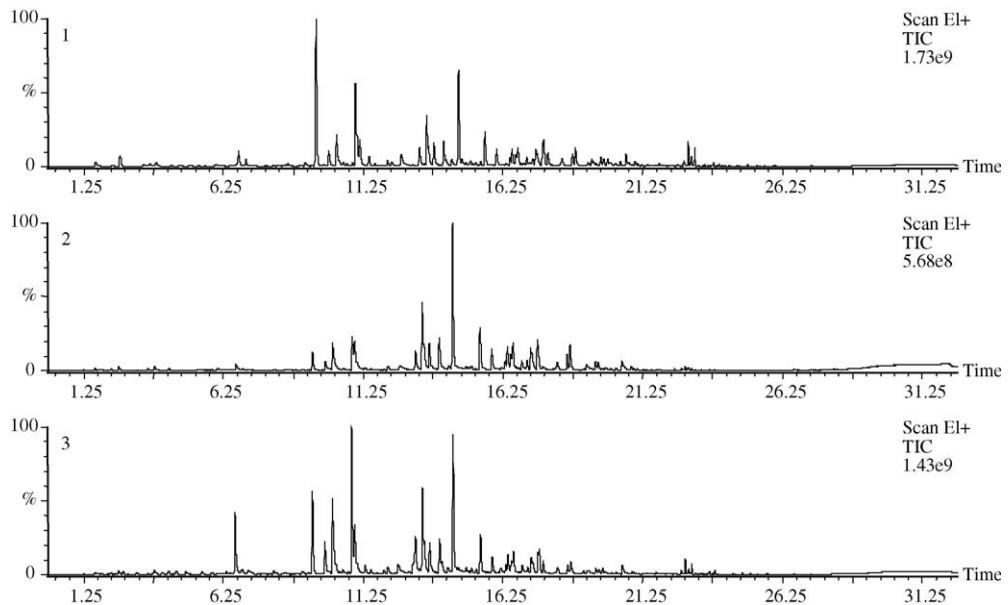


Fig. 9. Exemplary chromatograms obtained as a result of analysis of remains of carpet ignited using unleaded gasoline and distinguished by water after 60 min. Burning was conducted at three different levels of air accessibility—lowest (chromatogram 1), medium (chromatogram 2) and highest air accessibility (chromatogram 3).

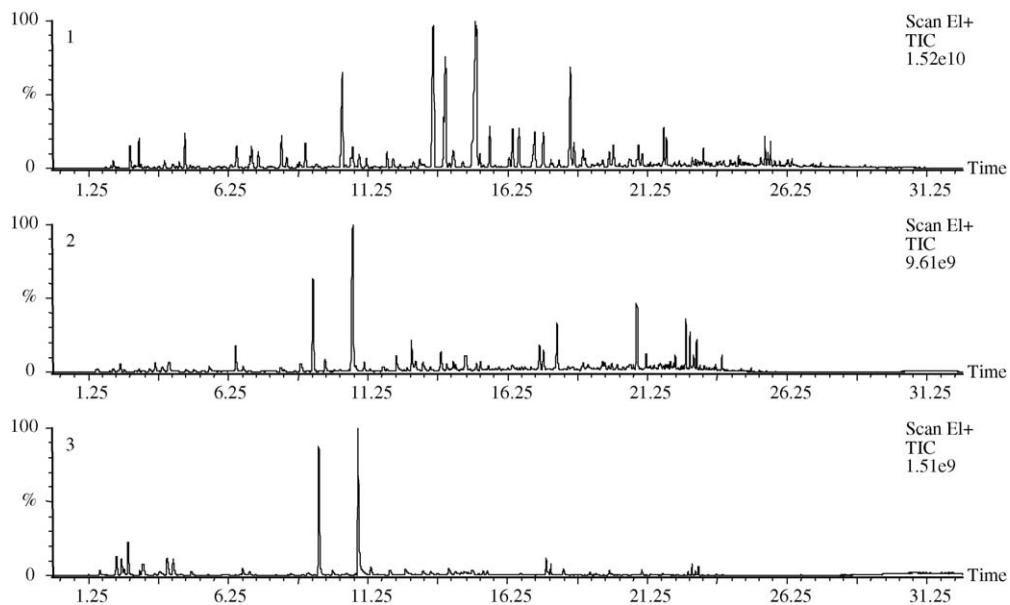


Fig. 10. Exemplary chromatograms obtained as a result of analysis of remains of carpet ignited using extraction solvent and distinguished by water after 60 min. Burning was conducted at three different levels of air accessibility—lowest (chromatogram 1), medium (chromatogram 2) and highest air accessibility (chromatogram 3).

3.3. Experiments involving the burning of chipboard pieces using different accelerants and for different burning durations

The signal levels for all samples were at least one order of magnitude below the limit of detection. The signal levels for the first series of experiments and their repetition are similar, but the chromatograms are significantly different. What is interesting is that the level of signals obtained for analysis of the samples is even lower than that obtained for blank samples. It was also observed that during burning, the chipboard pieces were delaminating and in this way the inner layers were exposed to the effects of the fire. The only remains after burning were small charred particles, a few millimeters in size.

3.4. The influence of air availability on the results of fire debris analysis

Analyses of the samples from the experiments concerning the influence of air availability were conducted with high split settings (for most samples inlet split was set to $300 \text{ cm}^3/\text{min}$ and outlet split to $100 \text{ cm}^3/\text{min}$) to prevent column overloading. As a ‘side effect’ of this, the overall helium flow through the column was increased, and the retention time was shortened, which can be observed in the resultant chromatograms—the retention time for samples analysis is significantly shorter than for standard chromatograms of given accelerants.

For all investigated accelerants, except the extraction solvent, characteristic profiles of chemical compounds are recognizable, regardless of the air availability level. In the case of the extraction solvent, chromatograms are not

recognizable for any of the air availability levels, although the chromatograms are similar to each other.

The chromatograms obtained for diesel fuel remain recognizable, but differ slightly for different samples. In all experiments, the same brand of diesel fuel (ORLEN) was used. The most probable reason for observed differences is the change in fuel composition.

For gasoline, differences in quantitative ratios of C2 alkyl derivates of benzene (ethylbenzene, *p*, *m*-xylene and *o*-xylene) can be observed. This can be explained by the influence of fire conditions or, more probably, by changes in gasoline composition [6]. Still, the characteristic pattern of C3 and C4 alkyl derivates, considered being gasoline’s ‘fingerprint’, remains unchanged, enabling identification.

4. Conclusions

4.1. The influence of the time between ignition and extinguishing of fire, type of accelerant and type of burned material on the possibility of detection and identification of accelerants traces

The results of conducted examinations show that among investigated factors, the kind of burned material is the most important.

For carpet, regardless of the burning time (within the investigated range of times), traces of used accelerants (except the highly volatile extraction solvent) were easily recognizable. As for the deciduous wood, traces of

accelerants were only detectable in a few samples. In the case of the chipboard samples, none of the used accelerant was detected after the allowed time of burning. The type of accelerant used and the time of burning have less significance.

Observations made during the experiments allow us to draw the following general conclusions: some plastic materials, such as the carpet used in this research, show a tendency to spontaneous extinguishing before complete incineration, if some additional heat is not provided. The inner layers are isolated from the open air by an exterior layer of charred material. That is why, accelerants traces (except the most volatile ones) are easily detectable in the debris of such materials, irrespective of the length of time between ignition and collecting of samples. Other burned materials, such as wood or chipboard, if not extinguished, glow until complete incineration and no accelerant traces remain.

It is probable that the described phenomenon (spontaneous extinguishing of plastics materials) is specific for conditions similar to those of the described experiments and will not occur in full-scale fires where additional heat is provided from other burning materials.

The amount of accelerant traces in fire debris is also determined by factors other than those investigated, such as the arrangement of burned materials or spread of accelerants on burned materials. These factors, although difficult to regulate, influence the conditions of combustion (e.g. the maximal operative temperature) and thereby the amount and composition of accelerant traces left.

4.2. The influence of air availability

The conducted research shows that changes in air availability do not significantly influence the possibility of detection of accelerants traces. Regardless of the degree of air availability, the phenomenon described above was observed—on the burning carpet a kind of shield composed of charred material formed, isolating the inner layers from the open air. The fire goes out spontaneously approximately 40 min after ignition, though the inner layers remained unburned.

It is possible that obtained results are characteristic for the investigated material only (carpet made from plastic) and cannot be applied to other types. It is very probable that if some other material (e.g. wood) were used, an increase in air

availability would lead to a decrease in the amount of accelerant traces, which intuitively seems to be obvious.

The obtained results clearly show the importance of blank samples in accelerant analysis, especially when carried out with the use of a detector with such a low detection limit as the mass spectrometer. The blank samples allow determination of the signal level below which compound signals should be treated as insignificant. The conducted analyses show that though the jars and lids used for sample collection were carefully washed and pre-heated before use, during the heating of samples they released compounds which could be mistaken for some paint thinners or even highly evaporated gasoline traces. By carrying out analysis of blank samples with each series of analyzed samples, false positive results of identification can be avoided.

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